



Study of a novel porous gel polymer electrolyte based on thermoplastic polyurethane/poly(vinylidene fluoride-co-hexafluoropropylene) by electrospinning technique



Ling Zhou, Qi Cao*, Bo Jing, Xianyou Wang, Xiaoli Tang, Na Wu

Key Laboratory of Environmentally Friendly Chemistry and Applications of Minister of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China

HIGHLIGHTS

- Prepare PVDF-HFP/TPU gel polymer electrolyte by electrospinning the first time.
- The ionic conductivity of the GPE is $4.1 \times 10^{-3} \text{ S cm}^{-1}$.
- The membrane has a high tensile strength (8.38 MPa) and elongation (118.7%).
- The PVDF-HFP/TPU GPE is very suitable for polymer lithium ion batteries.

ARTICLE INFO

Article history:

Received 20 January 2014

Received in revised form

26 March 2014

Accepted 28 March 2014

Available online 18 April 2014

Keywords:

Thermoplastic polyurethane

Poly(vinylidene fluoride-co-

hexafluoropropylene)

Gel polymer electrolyte

Electrospinning

ABSTRACT

A novel electrospun gel polymer electrolyte (GPE) consisting of thermoplastic polyurethane (TPU) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is prepared and investigated. Its characteristics are investigated by scanning electron microscopy (SEM), thermal analysis (TGA). The GPE shows a maximum ionic conductivity of $4.1 \times 10^{-3} \text{ S cm}^{-1}$ with electrochemical stability up to 5.5 V versus Li^+/Li at room temperature. In addition, it shows a first charge–discharge capacity of 168.8 mAh g^{-1} when the gel polymer electrolyte (GPE) is evaluated in a Li/PE/LiFePO_4 cell under 0.1 C-rate at the first cycle. What's more, there is microscale attenuation (1%) in the 30 cycles of charge and discharge tests. The TPU/PVDF-HFP membrane has a high tensile strength ($8.4 \pm 0.3 \text{ MPa}$) and elongation at break ($118.7 \pm 0.2\%$). With the outstanding electrochemical and mechanical performance, it is very suitable for application in polymer lithium ion batteries.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Lithium ion battery has been studied widely and deeply in the energy sources rapid growth time, especially the electrode material. As we all know, superior performance of lithium ion battery is determined by active electrode material and excellent electrolytes. The GPEs have been reported with sufficient mechanical strength, high ionic conductivity at room temperature, stable and well compatibility with lithium electrodes [1–3]. There are many ways to produce GPEs such as phase inversion method, γ -ray irradiation method, solvent casting technique, TIPS technique, and electrospinning technique, in order to improve the ionic conductivity [4,5].

Among these methods, electrospinning technique which made the solution of polymer into lots of uniform and slender nanofibers by high voltage is a simple, controllable and efficient approach [6]. Choosing appropriate high molecular polymer is also extremely important for the property of GPEs. TPU contains two-phase microstructure which are soft segments and hard segments [7,8]. The hard sections are incompatible with the soft section in thermodynamics, while these two phases are interconnected throughout each other. The whole system benefit from these two phases since that the hard part afford spatial stability and the soft phases are conducive to good ionic conductivity owing to the soft segments didn't form ionic cluster after being dissolved alkali metal. Many investigations were devoted to copolymerize TPU with other polymer for processing GPEs. Some article on based of coaggregant like thermoplastic polyurethane (TPU)/linear poly(ethylene oxide) (PEO) (TPU-PEO), thermoplastic polyurethane (TPU)/polyacrylonitrile (PAN) (TPU-PAN) and polyurethane/poly

* Corresponding author. Tel./fax: +86 731 58298090.
E-mail address: wjcaqi@163.com (Q. Cao).

(vinylidene fluoride) (PU-PVDF) as GPEs for rechargeable lithium batteries have been reported lately [9–11]. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has been as the matrix of polymer electrolytes in lithium ion batteries [12]. Making a comparison copolymers between PVDF and PVDF-HFP, the latter in the gel owns lower glass transition temperature, greater solubility for organic solvents and less crystallinity [13]. Accordingly, there are more amorphous domains in PVDF-HFP which could absorb greater amounts of liquid electrolytes, and enough mechanical integrity profiting from the crystalline regions is conducive to prepare free-standing membrane as well [12,14,15]. There is no microphase separation of mingling between PVDF-HFP and TPU as electrospun matrix for the GPEs. This due to the structure of PVDF-HFP and TPU, the functional group (–C–F) in the backbone structure of PVDF-HFP which is strong electron-withdrawing can product hydrogen bonds with amino-group (–NH) in the hard segments of TPU. Therefore, the GPEs based on PVDF-HFP and TPU possess high ionic conductivity and fine mechanical stability at ambient temperature [6].

In this paper, we report for the first time on a novel electrospun membrane prepared from PVDF-HFP and TPU mixture solution. Therefore, we make TPU/PVDF-HFP mixture solution, pure TPU and pure PVDF-HFP solution into three different membranes. And then the nonwoven films immerse into 1 M LiClO₄-EC/PC liquid electrolyte solution for being activated at room temperature in a glove box. The performance of electrospun membranes prepared by TPU/PVDF-HFP mixture is observed to be comparatively better than the one made by pure TPU or pure PVDF-HFP. In addition, the GPE of TPU/PVDF-HFP shows a high ionic conductivity of $4.1 \times 10^{-3} \text{ S cm}^{-1}$ with electrochemical stability up to 5.5 V versus Li⁺/Li and first charge–discharge capacity of 168.8 mAh g^{−1}, with LiFePO₄ as cathode material. The TPU/PVDF-HFP film gets the longest elongation 118.8%, with the max breaking tensile strength 8.38 MPa. Both the tensile strength and elongation at break are excellent.

2. Experimental

2.1. Materials

Poly (vinylidene difluoride-co-hexafluoropropylene) (PVDF-HFP, Knyar Flex, LBG) and Thermoplastic polyurethane (TPU, yantaiwanhua, 1190A) were dried under vacuum at 80 °C for 24 h. LiClO₄·3H₂O (AR, Sinopharm Chemical Reagent Co., Ltd) was dehydrated in vacuum oven at 120 °C for 72 h. 1.0 M Liquid electrolyte was made by dissolving a certain quality of LiClO₄ in ethylene carbonate (EC, Shenzhen capchem technology Co., Ltd)/propylene carbonate (PC, Shenzhen capchem technology Co., Ltd) (1/1, v/v). *N,N*-Dimethylformamide (DMF) and acetone were analytical purity and used as received without further treatment.

2.2. Preparation of TPU/PVdF-HFP, TPU and PVDF-HFP fibrous membrane

Firstly a certain amount of TPU and PVdF-HFP powder (50/50, wt/wt) were homogeneously dissolved in the mixture of an acetone/*N,N*-dimethylacetamide (1:1, wt/wt) forming a 9 wt % solution. Totally, 9 wt % pure TPU solution and 9 wt % pure PVDF-HFP solution were made by the same way, severally. The solution was electrospun under high voltage of 24.5 kV and tip-to-collector distance of 15 cm at room temperature, respectively. Porous fibrous films were obtained on the collector plate. The electrospun porous fibrous films were finally dried under vacuum at 80 °C for 12 h.

2.3. Preparation of gel polymer electrolytes

The thickness of the TPU/PVdF-HFP nonwoven films used was ~100 μm. At room temperature, the dried TPU/PVdF-HFP, pure TPU and pure PVDF-HFP nonwoven films were activated by dipping in 1 M LiClO₄-EC/PC liquid electrolyte solutions for 1 h in a glove box filled with argon. Wipe the surface of swelled membranes by filter paper and then get gel polymer electrolytes.

2.4. Membrane characterization

Scanning electron microscope (SEM, Hitachi S-3500 N, Japan) was used to examine the morphology of films. The TPU/PVdF-HFP porous fibrous films were gold sprayed prior to SEM measurements. The thermal stability of the films was monitored using thermogravimetric analysis (model TGAQ 50, TA Company, USA). The TGA measurements were carried out under dry nitrogen atmosphere at a heating rate of 20 °C min^{−1} from 30 to 900 °C. The mechanical strength of the polymer gel electrolyte films was measured by universal testing machines (UTM, Instron Instruments). There are some difficulties in surveying the “wet” films (with electrolyte), therefore the test was measured mechanical properties of the “dry” membrane (without electrolyte). The extension rate was kept at ~5 mm min^{−1}. The dimensions of the sheet used were ~2 cm × 5 cm × ~150–250 μm (width × length × thickness). The ionic conductivity of the composite film was measured with SS/PE/SS blocking cell by AC impedance measurement using Zahner Zennium electrochemical analyzer with a frequency range of 0.1–1 MHz. The thin films were prepared about 100 μm in thickness and 1.96 cm² in area for impedance measurement. Thus, the ionic conductivity could be calculated from the following equation:

$$\sigma = \frac{h}{R_b S} \quad (\text{A})$$

In Eq. (A), σ is the ionic conductivity, R_b is the bulk resistance, h and S is the thickness and area of the films, respectively.

The porosity was investigated by immersing the membranes into *n*-butanol for 1 h and then calculated by using the following relation:

$$P = \frac{W_w - W_d}{\rho_b V_p} \times 100\% \quad (\text{B})$$

where W_w and W_d are the mass of the wet and dry membrane, respectively, ρ_b the density of *n*-butanol, and V_p the volume of the dry membrane.

The electrolyte uptake was determined by measuring the weight increase and calculated according to Eq. (C):

$$\text{Uptake (\%)} = \frac{W - W_0}{W_0} \times 100\% \quad (\text{C})$$

where W_0 is the weight of dried films and W is the weight of swelled films.

2.5. Cell assembly and performance characteristics

Electrochemical stability was measured by a linear sweep voltammetry (LSV) of a Li/PE/SS cell using Zahner Zennium electrochemical analyzer at a scan rate of 5 mV s^{−1}, with voltage from 2.5 V to 6 V. For charge–discharge cycling tests, the Li/PE/LiFePO₄ cell was assembled. The cell was subjected to electrochemical performance tests using an automatic charge–discharge unit, Neware

battery testing system (model BTS-51, ShenZhen, China), between 2.5 and 4.2 V at 25 °C, at different current densities.

3. Results and discussion

3.1. Morphology and structure

Fig. 1 shows the SEM images of the membranes prepared by electrospinning of polymer solution (pure TPU, pure PVDF-HFP, and TPU/PVDF-HFP). All of these three membranes show a microporous structure and the TPU/PVDF-HFP membrane fibers appear to be uniform in composition without having any microphase separation

due to the miscibility of TPU and PVDF-HFP. The fibers of pure TPU (Fig. 1(a)) crosslinked very stickily and unevenly, with the diameter distribution values range between 100 nm and 2500 nm, with an average fiber diameter of ~ 1200 nm. The fibers of pure PVDF-HFP (Fig. 1(b)) are relatively homogeneous and slender, with the diameter distribution values range between 100 nm and 400 nm, with an average fiber diameter of ~ 250 nm, but there are some floccule in the membrane. While the fibers of mix TPU and PVDF-HFP (Fig. 1(c)) are quite uniform and slender, with the diameter distribution values range between 200 nm and 400 nm, with an average fiber diameter of ~ 300 nm.

There are different appearance defects in pure TPU and pure PVDF-HFP films, but the mixed TPU and PVDF-HFP films not only coalesce both advantages but also avoid their drawbacks, thereby the mix films acquire superior electrochemical performance and decent mechanical property as followed.

3.2. Thermal analysis

Thermograms of membranes with different compositions are shown in Fig. 2. The pure TPU membrane and the mix TPU and PVDF-HFP films both start to lose weight at about 350 °C, and the pure TPU membrane has 2% weight left at 500 °C while the mix TPU and PVDF-HFP films had lost 70% mass at 530 °C. But the pure PVDF-HFP diaphragm losses weight from 490 °C to 530 °C with 65% mass reduced.

With the content of PVDF-HFP added, the film becomes more stable. This may due to the strong interaction between the two polymer matrixes (TPU and PVdF-HFP). The addition of PVdF-HFP causes the interaction between its fluorine groups with carbonyl (C=O) and amino-group (–NH) in TPU. Thus the interaction of the two polymer chains would be stronger and the PVdF-HFP chains would restrict the movement of the TPU chains during the glass transition. This enhances the compatibility of TPU and PVdF-HFP.

3.3. Electrolyte uptake and ionic conductivity

Fig. 3 shows the uptake behavior of the electrospun fibrous membranes. The percentage of electrolyte uptake can be calculated according to Eq. (B). The pure TPU fibrous film shows an electrolyte uptake of about 135% within 2 min, while the pure PVDF-HFP membrane is 210% and TPU/PVdF-HFP film is 323%. After 15 min, it is found that when the electrolyte uptake of these three curves become stabile. The uptake of the electrolyte solution reaches up to 175% [TPU], 341% [TPU/PVdF-HFP] and 304% [PVdF-HFP], respectively. The membrane with TPU/PVdF-HFP always owns the highest electrolyte uptake percentage. The absorption of large quantities of liquid electrolyte by the composite membranes results from the high porosity of the membranes and the high amorphous content of the polymer. The fully interconnected pore structure makes fast penetration of the liquid into the membrane possible, and hence the uptake process is stabile within the initial 15 min. TPU/PVdF-HFP membrane owns the highest porosity, so it always has the highest electrolyte uptake percentage. Furthermore the decreasing of the average fiber diameters from 1.2 μm [TPU] to 0.3 μm [TPU/PVdF-HFP] also leads to the increasing in the absorption ratio of the electrolyte solution from 175% to 341%. Because the porosity and the surface area of the pore wall of the film will be increasing with the average fiber diameters decreasing. The increasing of surface area of the pore wall and more pores result in a higher uptake of the liquid electrolyte, which means more Li^+ in the same volume. This leads TPU/PVdF-HFP polymer electrolyte to have a high ionic conductivity.

Fig. 4 shows the impedance spectra of TPU/PVdF-HFP based fibrous polymer electrolyte. It is typical AC impedance for gel

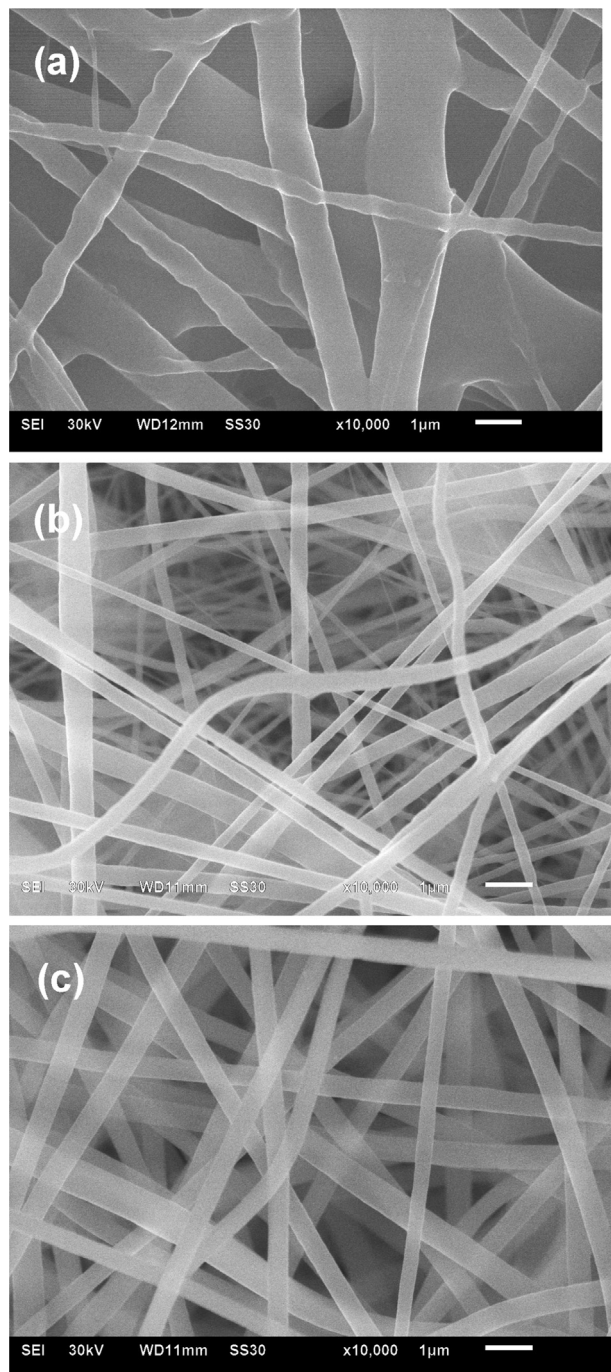


Fig. 1. SEM images of electrospun membranes (a) TPU (b) PVdF-HFP (c) TPU/PVdF-HFP.

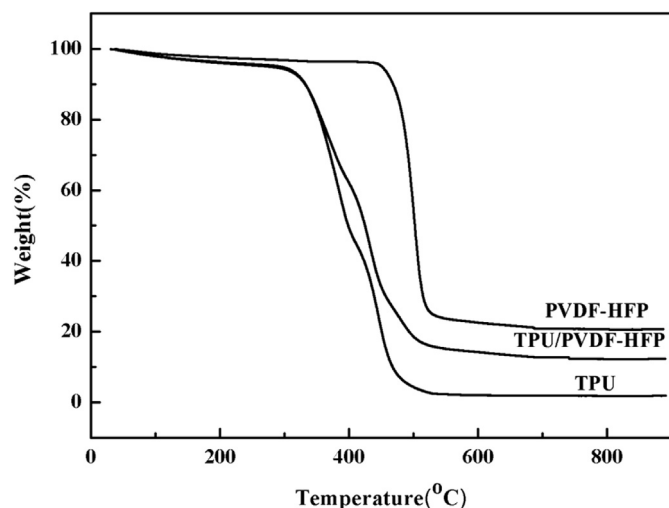


Fig. 2. Thermograms of TPU/PVdF-HFP films.

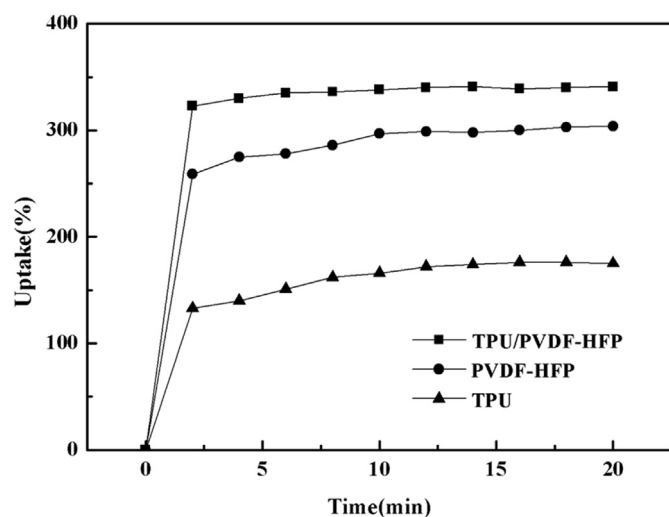


Fig. 3. The uptake behavior of the electrospun fibrous films.

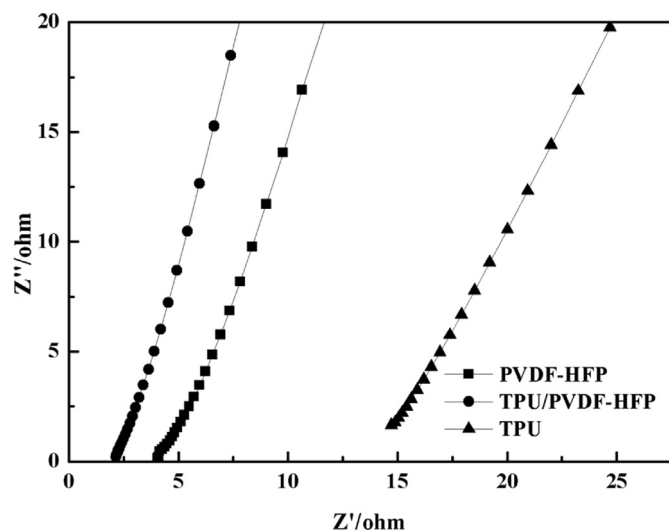


Fig. 4. Impedance spectra of gel polymer electrolytes.

polymer electrolyte. From the morphology of the prepared porous electrospun TPU/PVdF-HFP membranes in Fig. 1, it is known that there are many interconnected pores in the porous membranes, so enough liquid electrolyte was absorbed by the polymer membrane to form gelled polymer electrolyte. The pores are also interconnected by the sub-micron windows, which offer channels for the migration of ions and are small enough to well retain the electrolyte solution in the membrane. Obviously, the higher electrolyte-solution uptake is, the more Li^+ ions are in gelled polymer electrolyte. As we all know ions are the current carriers. This may be the reason for the high frequency semicircular disappearing in the impedance spectra. And this leads to a further conclusion that the conductivity is mainly the result of ion conduction [16]. It can be observed clearly from Fig. 4 that the bulk resistance (R_b) of the TPU fibrous polymer electrolyte is 14.71Ω . And in Fig. 4 the PVdF-HFP has a bulk resistance of 4.08Ω . However, in Fig. 4 the bulk resistance (R_b) of the TPU/PVdF-HFP fibrous polymer electrolyte is only 1.85Ω . The decrease in the average fiber diameters leads to the increase in the absorption ratio of the electrolyte solution. And a higher uptake of the liquid electrolyte, which means more Li^+ in the same volume, leads to a lower bulk resistance (R_b). Though the data in Table 1, the ionic conductivity could be calculated with Eq. (A). The ionic conductivity of TPU and PVdF-HFP fibrous polymer electrolyte is $4.2 \times 10^{-4} \text{ S cm}^{-1}$ and $2.1 \times 10^{-3} \text{ S cm}^{-1}$, respectively. However the TPU/PVdF-HFP fibrous polymer electrolyte film has an ionic conductivity of $4.1 \times 10^{-3} \text{ S cm}^{-1}$.

3.4. Evaluation in Li/LiFePO₄ cell

Fig. 5(a) shows the first charge–discharge capacity curves of the cells with GPEs of TPU/PVdF-HFP. The charge–discharge curves are similar to what is observed in lithium ion batteries in general, which ensures a good contact between the electrodes and TPU/PVdF-HFP based GPEs. The GPEs with TPU delivers a charge capacity of 132.7 mAh g^{-1} and discharge capacity of 130.1 mAh g^{-1} , only 78% of the theoretical capacity of LiFePO_4 . PVdF-HFP gel polymer electrolyte delivers a charge capacity of 146.5 mAh g^{-1} and discharge capacity of 144.9 mAh g^{-1} . The TPU/PVdF-HFP composite polymer electrolyte shows a charge capacity of 168.8 mAh g^{-1} and discharge capacity of 167.5 mAh g^{-1} , which is about 99% of the theoretical capacity. This could be the result of reduced the compatibility of TPU and PVdF-HFP in polymer matrix. As to detailed reasons, further study is under way. From the results, we can find the TPU/PVdF-HFP based GPEs delivers a charge–discharge capacity of 168.8 mAh g^{-1} .

Upon that we studied the charge–discharge capacity of the cell with GPEs of TPU/PVdF-HFP at different current rates, the results can be seen from Fig. 5(b). It is noted that the charge and discharge capacities of LiFePO_4 are 168.8 and $167.82 \text{ mAh g}^{-1}$ at 0.1 C , exceed in 99% and 98% of theoretical capacity of 170 mAh g^{-1} for LiFePO_4 , indicating exceptionally high electrochemical performance conversion of this membrane material. Although the discharge capacities decrease with the increasing current rates due to the higher polarization at higher current densities, the anode material still exhibits high discharge capacities of 164 , 159 and 154 mAh g^{-1} .

Table 1
Surface area, height and porosity of fibrous membranes.

| Samples | Surface area (cm^2) | Height (cm) | Porosity (%) |
|--------------|--------------------------------|-------------|--------------|
| TPU | 1.958 | 0.012 | 52 |
| PVdF-HFP | 1.901 | 0.016 | 79 |
| TPU/PVdF-HFP | 1.845 | 0.014 | 88 |

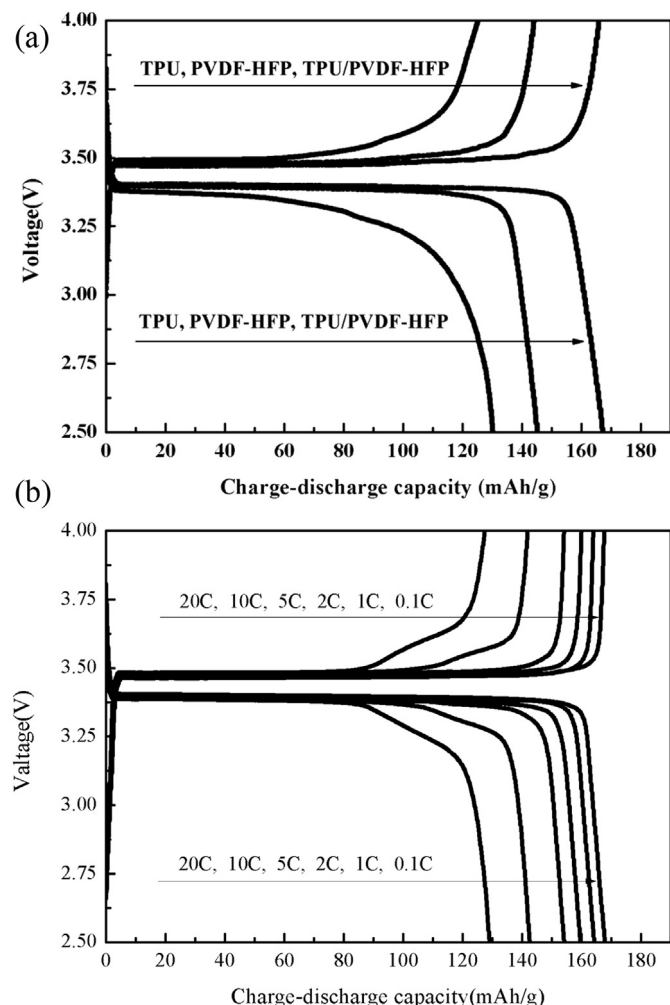


Fig. 5. (a) First charge–discharge capacities of GPEs based on electrospun TPU/PVDF-HFP membrane. (b) First charge–discharge capacities of GPEs based on electrospun TPU/PVDF-HFP membrane at different capacity rate (1 C = 170 mAh g⁻¹).

at relatively smaller current rates of 1, 2 and 5 C. Even at much higher current rates of 10 and 20 C, competitive capacities of 142 and 129 mAh g⁻¹ for anode material can be achieved, suggesting that GPEs of TPU/PVdF-HFP possesses superior electrochemical performance.

The Li cell with GPEs has been evaluated for cycle ability property under the 0.1 C rate at 25 °C and the results are shown in Fig. 6(a). Compared to the cells with GPEs containing TPU and PVDF-HFP in Fig. 6(a), the cell with TPU/PVdF-HFP based GPEs in Fig. 6(a) has a highest discharge capacities in the whole 30 cycles and exhibits the significantly improved cycle performance. The capacity retention after 30 cycles is found to be 98% for the TPU/PVdF-HFP based GPEs, 84% and 87% for the TPU and PVdF-HFP based GPEs, respectively. There is no evident capacity fading of the cell with TPU/PVdF-HFP based GPEs after a few cycles. This suggests that the cell exhibits a better reversibility. May be it results from a better stabilization of the system as a whole. This study shows that electrospun TPU/PVdF-HFP based GPEs is very suitable for Li/LiFePO₄ cells under low current densities (0.1 C) at room temperature.

At the same time, The cycle performance of cell with GPEs of TPU/PVDF-HFP at different current rates from 0.1 to 20 C illustrated in Fig. 6(b). At lower current rates (1 C), the capacity retentions are close to 100% after 30 cycles. Even at high-rate of 20 C, the capacity

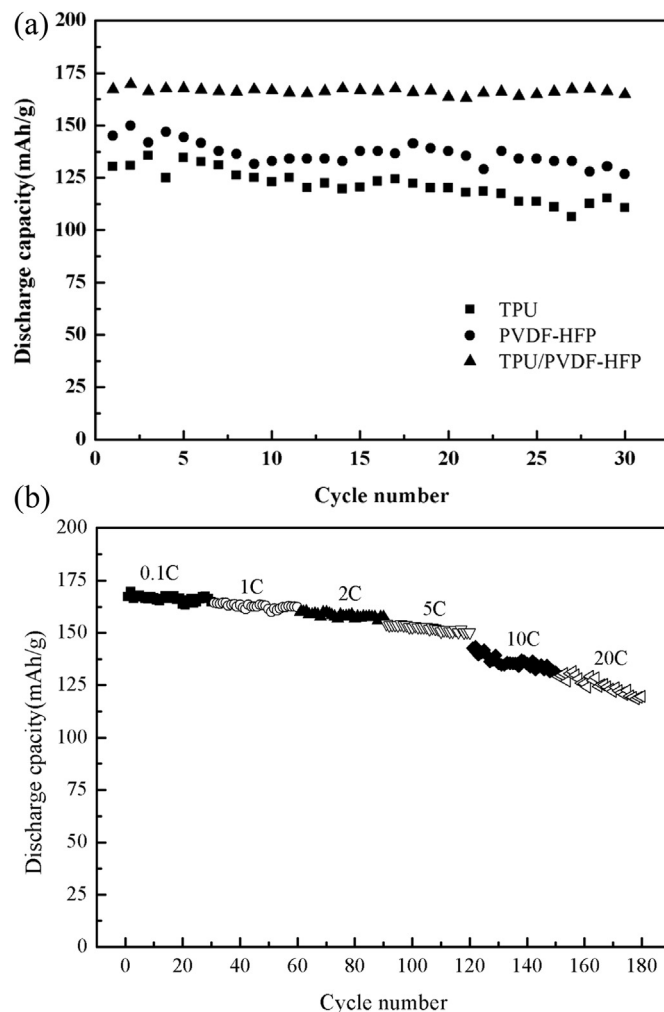


Fig. 6. (a) The cycle performance (discharge capacities) of GPE based on electrospun TPU/PVdF-HFP membranes. (b) The cycle performance (discharge capacities) of GPE based on electrospun TPU/PVdF-HFP membranes at different capacity rate.

retention is as high as 92.7% and the cell still remains a discharge capacity of 119 mAh g⁻¹ after 30 cycles. The outstanding electrochemical performance of GPEs is attributed to the particular morphology and structure of TPU/PVDF-HFP that the nanofibers, high porosity and no microphase separation of mingling between PVDF-HFP and TPU.

3.5. Mechanical property

Fig. 7 shows the stress–strain curves of the polymer membranes. The results of mechanical strength test show that the hybrid fillers improved the mechanical performance of membranes. The pure PVDF-HFP membrane extended only 48.2% with the max breaking tensile strength 3.86 MPa. Referring to the pure TPU film, the membrane has 65.5% elongation and been broken under the 8.55 MPa tensile strength. While the mixed films owes the longest elongation 118.8%, it can bear the tensile strength below 8.38 MPa. In a word, both the tensile strength and elongation of the mixed films at break are excellent. The reasons are as below. The copolymers fabricate by TPU and PVDF-HFP are homogeneous and symphysic. There is no microphase separation of miscible between PVDF-HFP and TPU as electrospun films. Thus it has a great contact area with the polymeric matrix. When the material is

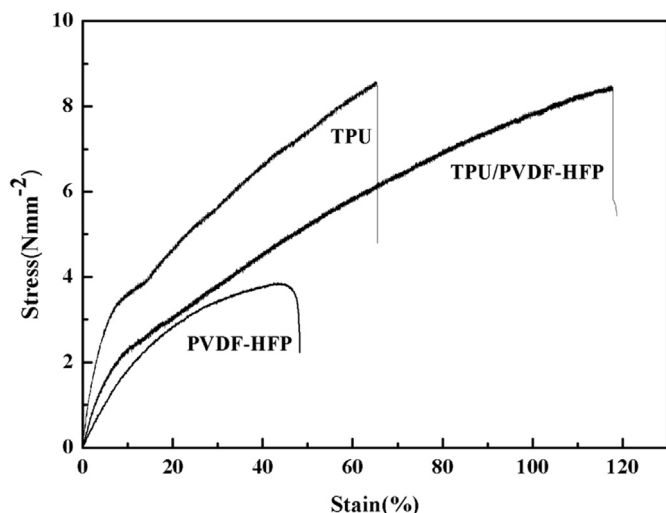


Fig. 7. Stress–strain curves of the electrospun TPU/PVdF-HFP membranes.

struck, the more microcracking will absorb more impact energy. So the further expansion of the cracks is blocked. Elongation at break often reflects the impact performance of material and the impact resistance is shown by the material toughness. The higher toughness in mechanical properties will reduce the risk of the collapse of the membrane, which suggests that the membrane prepared through copolymers TPU and PVdF-HFP is more suitable for application in polymer lithium ion batteries.

3.6. Electrochemical stability

The results of electrochemical stability tests of the gel polymer electrolytes by LSV are shown in Fig. 8. The electrochemical stability is at 4.5 V for the gel polymer electrolyte with pure PVdF-HFP electrolyte. With the addition of the TPU, the stability of the TPU/PVdF-HFP gel polymer electrolyte is further enhanced. Their electrochemical stability follows the order: membrane of pure PVdF-HFP (4.5 V) < pure TPU (5.1 V) < TPU/PVdF-HFP (5.5 V). From Fig. 8, we can see clearly that the gel polymer electrolyte of TPU/PVdF-HFP shows the best electrochemical stability. A decomposition process, which is associated with electrode/electrolyte, results

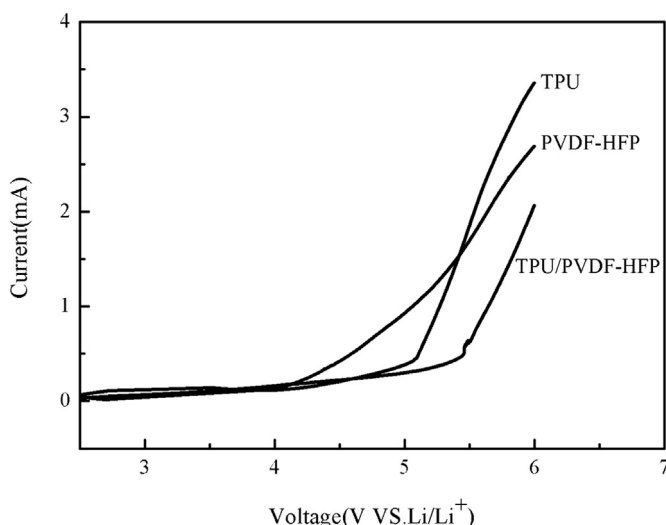


Fig. 8. Linear sweep voltammograms of the gel polymer electrolytes.

in the onset of current flow in the high voltage range. And this onset voltage is the upper limit of the electrolyte stability range. There is almost no electrochemical reaction in the potential range from 2.5 V to 5.5 V for TPU/PVdF-HFP gel polymer electrolyte. The beginning of current flow at 5.5 V represents the decomposition of the lithium electrode. A considerable current began to flow along with further increase of the cell voltage, indicating the onset of electrolyte decomposition process [17].

Therefore, the swollen phase of the membrane probably includes the complex compounds such as associated VdF-Li⁺ groups. This complex formation with lithium ion and VdF groups of PVdF-HFP enhances the electrochemical stability of GPEs. The electrochemical stability was also influenced by the high porosity, large and fully interconnected pores, the AFDs and uniform morphology of membranes. With the decreasing of AFDs, the oxidation stability of the GPE increased. So the gel polymer electrolyte of TPU/PVdF-HFP shows the best electrochemical stability.

These polymer electrolytes should render them very suitable for applications in lithium-ion battery because of the high anodic stability [18].

4. Conclusions

GPES based on fibrous TPU/PVdF-HFP blend/composite membranes were prepared by electrospinning the 9wt% polymer solution in DMF/acetone (1:1, w/w) at room temperature. The optimum blend composition has been observed for the electrolyte TPU/PVdF-HFP. TPU/PVdF-HFP based gel polymer electrolyte has a high ionic conductivity of $4.1 \times 10^{-3} \text{ S cm}^{-1}$ with electrochemical stability up to 5.5 V versus Li⁺/Li at room temperature. The first charge–discharge capacity of TPU/PVdF-HFP based gel polymer electrolyte lithium battery is about 168.8 mAh g⁻¹, which is about 99% of the theoretical capacity of LiFePO₄. The cell exhibits good compatibility with lithium electrodes. After 30 cycles the cell shows a very stable charge–discharge behavior and little capacity loss under current constant voltage conditions, at the 0.1 C-rate of 25 °C. The TPU/PVdF-HFP mixed films owes the longest elongation 118.8%, and it can bear the tensile strength below 8.38 MPa. Both the tensile strength and elongation are excellent. The above results indicate that the cell with TPU/PVdF-HFP based gel polymer electrolyte displays a superior potential and is very suitable for rechargeable lithium batteries.

Acknowledgments

The workers gratefully appreciate the financial supports from the Youth Project of National Nature Science Foundation of China (Grant No. 51103124 and No. 51203131) and Hunan Province Universities Innovation Platform of Open Fund Project (11K067).

References

- [1] J.J. Xu, H. Ye, *Electrochem. Commun.* 7 (2005) 829–835.
- [2] S.-I. Kim, H.-S. Kim, S.-H. Na, S.-I. Moon, Y.-J. Kim, N.-J. Jo, *Electrochim. Acta* 50 (2004) 317–321.
- [3] N. Wu, B. Jing, Q. Cao, X. Wang, H. Kuang, Q. Wang, *J. Appl. Polym. Sci.* 125 (2012) 2556–2563.
- [4] A. Manuel Stephan, N. Renganathan, S. Gopukumar, *Mater. Chem. Phys.* 85 (2004) 6–11.
- [5] N. Muniyandi, N. Kalaiselvi, P. Periyasamy, R. Thirunakaran, B.R. Babu, *J. Power Sources* 96 (2001) 14–19.
- [6] N. Wu, Q. Cao, X.Y. Wang, X.Y. Li, H.Y. Deng, *J. Power Sources* 196 (2011) 8638–8643.
- [7] M. Digar, S.-L. Hung, H.-L. Wang, T.-C. Wen, A. Gopalan, *Polymer* 43 (2002) 681–691.
- [8] J. Van Heumen, J. Stevens, *Macromolecules* 28 (1995) 4268–4277.
- [9] H.-H. Kuo, W.-C. Chen, T.-C. Wen, A. Gopalan, *J. Power Sources* 110 (2002) 27–33.
- [10] Y.-L. Du, T.-C. Wen, *Mater. Chem. Phys.* 71 (2001) 62–69.

- [11] P. Santhosh, T. Vasudevan, A. Gopalan, K.-P. Lee, *Mater. Sci. Eng. B* 135 (2006) 65–73.
- [12] W. Pu, X. He, L. Wang, C. Jiang, C. Wan, *J. Membr. Sci.* 272 (2006) 11–14.
- [13] S. Abbrent, J. Plestil, D. Hlavata, J. Lindgren, J. Tegenfeldt, Å. Wendsjö, *Polymer* 42 (2001) 1407–1416.
- [14] W. Ma, J. Zhang, X. Wang, S. Wang, *Appl. Surf. Sci.* 253 (2007) 8377–8388.
- [15] G.-L. Ji, B.-K. Zhu, Z.-Y. Cui, C.-F. Zhang, Y.-Y. Xu, *Polymer* 48 (2007) 6415–6425.
- [16] M. Jacob, S. Prabakaran, S. Radhakrishna, *Solid State Ionics* 104 (1997) 267–276.
- [17] Y.-X. Jiang, Z.-F. Chen, Q.-C. Zhuang, J.-M. Xu, Q.-F. Dong, L. Huang, S.-G. Sun, *J. Power Sources* 160 (2006) 1320–1328.
- [18] N. Wu, Q. Cao, X. Wang, S. Li, X. Li, H. Deng, *J. Power Sources* 196 (2011) 9751–9756.